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CRYSTALLINE LIQUIDS.*

By FRED B. PORTER, University of Kansas.

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CRYSTALLINE LIQUID is a term that has come into use to describe a phase in which a few substances have properties of both liquids and crystals. At certain temperatures these substances appear to the naked eye like ordinary liquids. They are free flowing, but have a cloudy or milky appearance. Under the polarizing microscope, however, they show double refraction, a property of crystals. At a higher temperature they suddenly lose the cloudiness and the double refractive powers and attain the true liquid phase. The temperature at which the solid changes to the cloudy liquid is the melting point, and the temperature at which the cloudiness disappears is called the transition point.

The first substance which was observed to have these peculiar properties was Cholesterine benzoate ($C_{36}H_{48}OOC C_6H_5$), (Schenck, Zeits. Phys. Chem. 25, 337). In 1887 Reinitzer, a German chemist, observed that this substance melted at 145° to a cloudy liquid, and that at 178° the cloudy appearance suddenly disappeared. He did not, however, observe its double refraction.

In 1890 three azoxyphenolethers, which had this cloudy modification of the liquid state, were made and studied by Gatterman (Be. 23, 1738). The composition, melting points and transition points of these substances are shown in the following table:

Name.	Formula.	Melting point.	Transition point.
Paraazoxyanisol,	$CH_3OC_6H_4-N \begin{array}{c} \diagup \diagdown \\ O \end{array} N-C_6H_4OCH_3$	114°	134.1°
Paraazoxyphenetol,	$C_2H_5OC_6H_4-N \begin{array}{c} \diagup \diagdown \\ O \end{array} N-C_6H_4OC_2H_5$	134.5°	164.2°
Anisolazoxyphenetol,	$CH_3OC_6H_4-N \begin{array}{c} \diagup \diagdown \\ O \end{array} N-C_6H_4OC_2H_5$	86°	116°

Gatterman also found that these substances, when exhibiting this cloudy appearance, have the property of double refraction. This he observed by means of a special apparatus for heating the substance under the polarizing microscope. Such an arrangement is necessary to observe the double refraction in the crystalline liquids thus far known, because none have been discovered that have the crystalline liquid phase at ordinary temperature.

The properties of the azoxyphenolethers have been further studied

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by Lehman (Zeits. Phys. Chem. 5, 427). He suspended drops of these substances in a medium of the same density, and found that the drops had two axes, as in solid crystals. The drops were rounded in form, but when two of these came in contact, instead of forming one drop with only two axes, four axes still remained. Pressing drops between glass plates did not destroy the axes, as might be expected.

The study of other physical chemical properties of these crystalline liquids has been carried on by Schenck. (Zeits. Phys. Chem. 25, 337). He determined their density at different temperatures, and found on plating the density curves that he obtained nearly straight lines, with the exception that at the transition point the density changes suddenly while the temperature remains constant, making a jog in the curve. The curves for all the crystalline liquids known are similar.

The molecular weight of the substances in the two liquid phases was found to be the same; that is, there is no change in the size of the molecules when the liquid passes through the transition point. We must have, then, two liquids which are chemically identical, but different in their physical properties, and, therefore, truly physical isomers. A curve showing the relation of the different phases of one of these substances could be drawn similar to the curve for sulphur. Sulphur has one vapor, one liquid and two solid phases, the monoclinic phase occupying a triangle (see Physical Chemistry, Walker), while a crystalline liquid has one vapor, two liquid, and one solid phase, the crystalline liquid phase occupying a triangle.

Such peculiar properties seemed worth observing, so we decided to make one of these substances. With the materials at hand, the preparation of *p*-azoxyanisole promised the best results. The compound from which *p*-nitrophenetole was made by Gatterman is now on the market, but as it could not be procured at once, it became necessary to make it. The *p*-nitrophenetole can be made (1) by treating *p*-phenetole with fuming nitric acid (Hallock, Am. 1, 271), or (2) by boiling *p*-nitrochlorbenzene with alcoholic potassium hydroxide solution (C. Willgerodt, Be. 15, 1002). The latter method was used. The *p*-nitrochlorbenzene was prepared from chlorbenzene, and the chlorbenzene from benzene itself.

For the preparation of chlorbenzene, benzene was chlorinated in the presence of aluminum turnings. The resultant liquid colored by decomposition products, contained varying amounts of the chlorbenzenes, which were separated by fractional distillation. The relative amounts of the mono-chlorbenzenes depended upon the amount of chlorine led into the benzene, and on the temperature during chlorination. The best results were obtained by warming the benzene until

it was evident that the reaction was beginning and then cooling it as soon as possible. In this way almost no black decomposition products and relatively more of the mono-chlorbenzene was obtained. In the fractional distillation, a part distils over below 90° . This was used in the next chlorination. The next fraction contains mono-chlorbenzene, b. p. 132° . At higher temperature, small amounts of dichlorbenzene, b. p. 172° , and of 1, 2, 3, 4-tetrachlorbenzene were obtained; and finally in one case, when the chlorination was carried too far, some higher distillations were obtained, even up to 300° ; but no other pure compounds were separated. It was necessary to repeat the fractional distillation at least seven times to separate the compounds.

Para-nitrochlorbenzene was next prepared (Riche A. 121, 357), by nitrating the chlorbenzene with fuming nitric acid at the temperature of ice-water. Both the ortho and para compounds are formed. At first the para compound was obtained pure by repeated crystallizations, but it was found later that an almost complete separation could be made by means of a Buchner funnel and the suction-pump. The ortho compound contains a considerable quantity of impurity, and is a liquid, and if pure it should melt at 32.5° . The para compound being solid, m. p. 83° , remains on the filter.

Paranitro-phenetol was then obtained (C. Willgerodt, Be. 15, 1002) by heating a mixture of 300 cc. alcohol, 150 cc. water, 10.5 g. potassium hydroxid, and 30 g. *p*-nitrochlorbenzene for thirty-six hours in a flask with a return condenser. The product obtained, after diluting with water and filtering, was purified by distillation with steam. The unchanged *p*-nitrochlorbenzene distils over first, followed by the *p*-nitrophenetol. A solid dichlorazoxybenzene, melting at 155° , and *p*-nitrophenol in solution remain in the flask.

Paraazoxyanisol was next prepared. Six g. sodium, 60 g. methyl alcohol, and 16 g. *p*-nitrophenetol (Schenck, Zeits. Phys. Chem. 25, 346), were sealed in tubes and heated for five hours at 110° , in the bomb furnace. The product, treated with alcohol, left a solid, which, when crystallized from chloroform, melted at 114° , and passed its transition point at 134° . As no microscope with heating stage was available, the double refraction of the paraazoxyanisol could not be observed by us.